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Supporting Information

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High Catalytic Activity of Heteropolynuclear Cyanide Complexes Containing Cobalt and Platinum Ions: Visible-Light Driven Water Oxidation**

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Experimental Method

Materials. All chemicals used for synthesis were obtained from chemical companies and used without further purification. $K_3[Co^{III}(CN)_6]$ was purchased from Stream Chemicals. $Co^{II}(NO_3)_2$ and $AgNO_3$ were supplied from Wako Pure Chemical Industries. $K_2[Pt^{IV}(CN)_6]$, $K_2[Pt^{II}(CN)_4]$, $Ru(bpy)_3Cl_2 \cdot 6H_2O$, and $Na_2S_2O_8$ were delivered by Sigma-Aldrich. Acetonitrile was obtained from Nacalai tesque. $[Ru(bpy)_3]SO_4$ was synthesized by a reported method.[S1] Purified water was provided by a water purification system, Millipore Direct-Q3 UV, where the electronic conductance was 18.2 MΩ cm.

Synthesis of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$. An aqueous solution (2.0 mL) containing calculated amounts of $K_2[Pt^{IV}(CN)_6]$ (0 – 85.8 mg) and $K_3[Co^{III}(CN)_6]$ (0 – 66.5 mg) was slowly added to an aqueous solution (1.0 mL) of $Co^{II}(NO_3)_2$ (87.3 mg, 0.30 mol) with magnetic stirring for 24 h at room temperature. The use of large excess amount of Co^{II} ions is necessary to avoid contamination of K^+ ions in products. The obtained pink powder was collected by centrifugation and washed with distilled water for two times. The obtained powder was dried in vacuo at room temperature. (Yield 37.4 – 50.5 mg, 55 – 98 %) The concentrations of Co and Pt were determined by XRF measurements. The ratio of Co and Pt in the starting solutions and those in the precipitates are listed in Table S1.

Table S1. Reaction conditions and chemical formula of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ determined by XRF measurements.

Molar ratio	Theoretical weight ratio in a product		Observed weight ratio		Expected formula based on the observed weight ratio
Co^{III}:Pt	Co^{II}+Co^{III}	Pt^{IV}	Co^{II}+Co^{III}	Pt^{IV}	
3:1	0.824	0.176	0.819	0.181	$[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}_{0.85}Pt^{IV}_{0.15})(CN)_6]$
1:1	0.555	0.455	0.566	0.434	$[Co^{II}(H_2O)_{1.33}]_{1.29}[(Co^{III}_{0.57}Pt^{IV}_{0.43})(CN)_6]$
1:3	0.368	0.632	0.390	0.610	$[Co^{II}(H_2O)_{0.80}]_{1.15}[(Co^{III}_{0.31}Pt^{IV}_{0.69})(CN)_6]$

Note: The average number of water molecules ligating to a Co(II) ion in a series of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ was estimated as follows: The basic units of the complexes are $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ and $Co^{II}[Pt^{IV}(CN)_6]$, both of which compensate the charges with octahedral coordination around Co(II) ions. When the molar ratio between the Co(III) and Pt(IV) complexes is (1–x):x in a complex, the

number of Co^{II} ions should be 1.5×(1–x) + x = 1.5–0.5x and the average number of the water molecules ligating to a Co^{II} ion is 3×(1–x)/(1.5–0.5x) in the complex.

Synthesis of $[Co^{II}(H_2O)_2]_n[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$. An aqueous solution (2.0 mL) containing calculated amounts of $K_2[Pt^{II}(CN)_4]$ (0 – 75.5 mg) and $K_3[Co^{III}(CN)_6]$ (0 – 66.5 mg) was slowly added to an aqueous solution (1.0 mL) of $Co^{II}(NO_3)_2$ (87.3 mg, 0.30 mmol) with magnetic stirring for 24 h at room temperature. The use of a large excess amount of Co^{II} ions is necessary to avoid contamination of K^+ ions in products. The obtained pink powder was collected by centrifugation and washed with distilled water for two times. The obtained powder was dried in vacuo at room temperature. (Yield 49 – 61 mg, 95 – 96 %) The concentrations of Co and Pt were determined by XRF measurements. The ratio of Co and Pt in the starting solutions and those in the precipitates are listed in Table S2.

Table S2. Reaction conditions and chemical formula of $[Co^{II}(H_2O)_2]_n[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ determined by XRF measurements.

Molar ratio	Theoretical weight ratio in a product		Observed weight ratio		Expected formula based on the observed weight ratio
Co^{III}:Pt^{II}	Co^{II}+Co^{III}	Pt^{II}	Co^{II}+Co^{III}	Pt^{II}	
3:1	0.824	0.176	0.808	0.192	$[Co^{II}(H_2O)_2]_{1.42}[\{Co^{III}(CN)_6\}_{0.84}\{Pt^{II}(CN)_4\}_{0.16}]$
1:1	0.555	0.455	0.612	0.388	$[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$
1:3	0.368	0.632	0.442	0.558	$[Co^{II}(H_2O)_2]_{1.20}[\{Co^{III}(CN)_6\}_{0.39}\{Pt^{II}(CN)_4\}_{0.61}]$

Note: The number of water molecules ligating to a Co(II) ion is always 2 in a series of $[Co^{II}(H_2O)_2]_n[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ by the following calculations: The basic units of a series of complexes are $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ and $[Co^{II}(H_2O)_2][Pt^{II}(CN)_4]$, both of which compensate the charges with octahedral coordination around Co(II) ions. When the molar ratio between the Co(III) and Pt(II) complexes was (1–x):x in a complex, the numbers of Co^{II} ions and water molecules should be 1.5×(1–x) + x = 1.5 – 0.5x and 3×(1–x) + 2x = 3 – x, respectively, in the complex. The molar ratio between Co(II) ions and water molecules is (1.5 – 0.5x):(3–x) = 1:2. Thus, the number of water molecules ligating to a Co(II) ion is 2 independent of x.

Physical Measurements. Powder X-ray diffraction patterns were recorded by a Rigaku MiniFlex 600. X-ray fluorescence measurements to determine the concentrations of Pt and Co were performed on a Rigaku ZSX 1000/MPS. UV-vis

diffused reflectance spectra were measured by a Jasco V-670 spectrometer equipped with an SIN-768 attachment. IR spectra were recorded on a Jasco FT/IR-6200 spectrometer for the samples pelletized with KBr. Nitrogen adsorption-desorption at 77 K was performed with an instrument for volumetric adsorption measurement, Belsorp-mini II (BEL Japan, Inc.), within a relative pressure range from 0.01 to 101.3 kPa. The mass of a sample was as much as ca. 50 mg for adsorption analysis after pretreatment at 393 K for ca. 4.0 h under vacuum conditions and kept in N_2 atmosphere until N_2-adsorption measurements. The sample was exposed to a mixed gas of He and N_2 with a programmed ratio and adsorbed amount of N_2 was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min). Cyclic voltammograms were recorded on an ALS electrochemical analyzer (Model 627 B) using an acetonitrile (2.0 mL) suspension of each complex (10 μmol).

Photocatalytic Water Oxidation. Photocatalytic oxygen evolution was performed as follows. A heteropolynuclaer cyanide complex (40 mg L^{-1}) was added to a phosphate buffer solution (50 mM, pH 8.0, 2.0 mL) containing $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]SO_4$ (1.0 mM) flushed with Ar gas. The solution was then irradiated with a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a color filter glass (Asahi Techno Glass) transmitting $\lambda > 420$ nm at room temperature. The concentration of oxygen gas in a headspace was quantified by a Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m × 0.53 mm) at 313 K] equipped with a thermal conductivity detector.

Reference

[S1] D. Hong, Y. Yamada, T. Nagatomi, Y. Takai, S. Fukuzumi, *J. Am. Chem. Soc.* **2012**, *134*, 19572-19575.

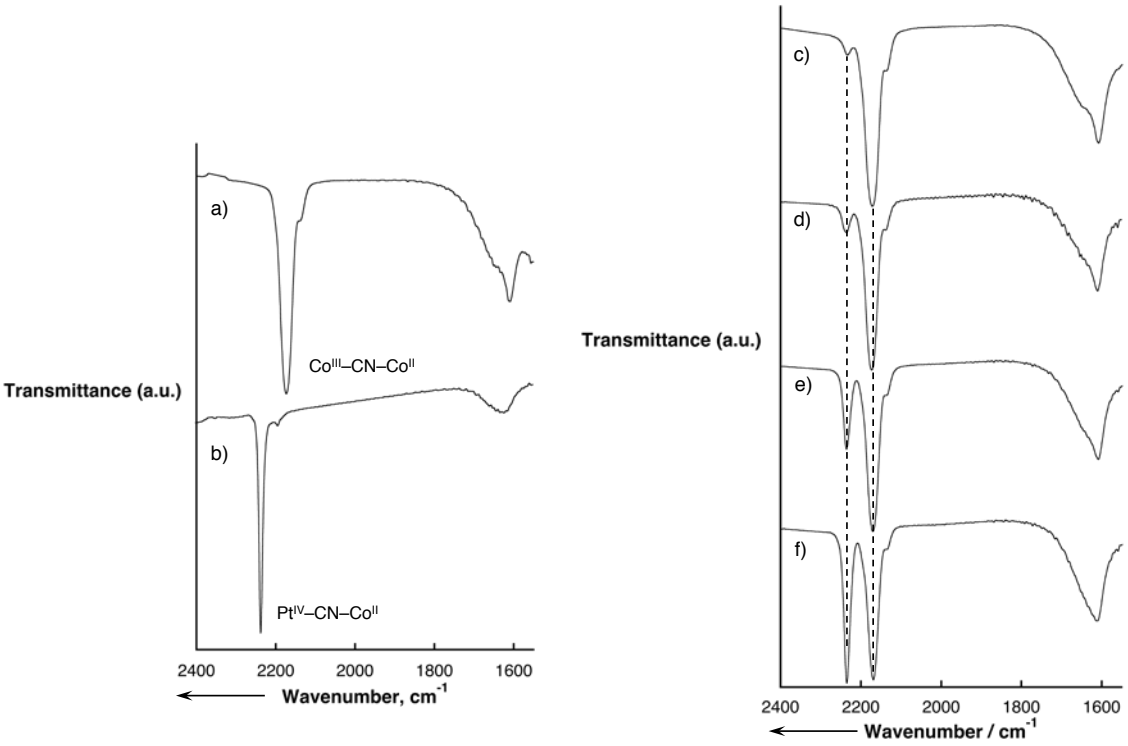

Figure S1. IR spectra of a series of hetero-polynuclear cyanide complexes, $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$. x = a) 0, b) 1, c) 0.10, d) 0.15, e) 0.43 and f) 0.69.

Comments: The CN stretching bands, ν(CN), observed in IR spectra has been reported to accurately reflect the coordination mode of the cyanide ligand. IR spectra measurements were conducted for the series of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$. From the IR spectra for $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ (x = 0) and $Co^{II}[Pt^{IV}(CN)_6]$ (x = 1), ν(CN) assignable to Co^{III}-CN-Co^{II} and Pt^{IV}-CN-Co^{II} appear at around 2175 and 2236 cm^{-1}, respectively. The ν(CN) shifted to higher wavenumber to 2236 cm^{-1} in Pt^{IV}-CN-Co^{II} resulted from more positively charged character of Pt^{IV} compared with Co^{III}. The HOMO of a cyanide ligand has an antibonding character, thus, more electron withdrawing character of Pt^{IV} strengthen the CN bond. IR spectra of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ (x = 0.10, 0.15, 0.43 and 0.69) in the ν(CN) region showed two peaks around 2175 and 2236 cm^{-1} which are assignable to Co^{III}-CN-Co^{II} and Pt^{IV}-CN-Co^{II}, respectively although the relative peaks intensities were varied depending on the concentration of Pt^{IV}.

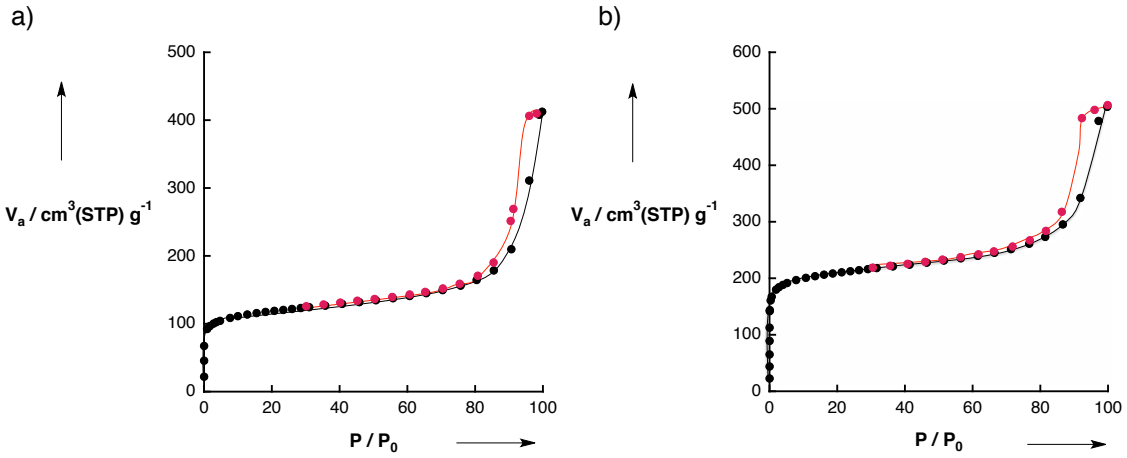

Figure S2. Typical examples of N_2 adsorption-desorption isotherm used for BET surface area determination. a) $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ (x = 0.43) and b) $[Co^{II}(H_2O)_2]_n[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ (x = 0.16).

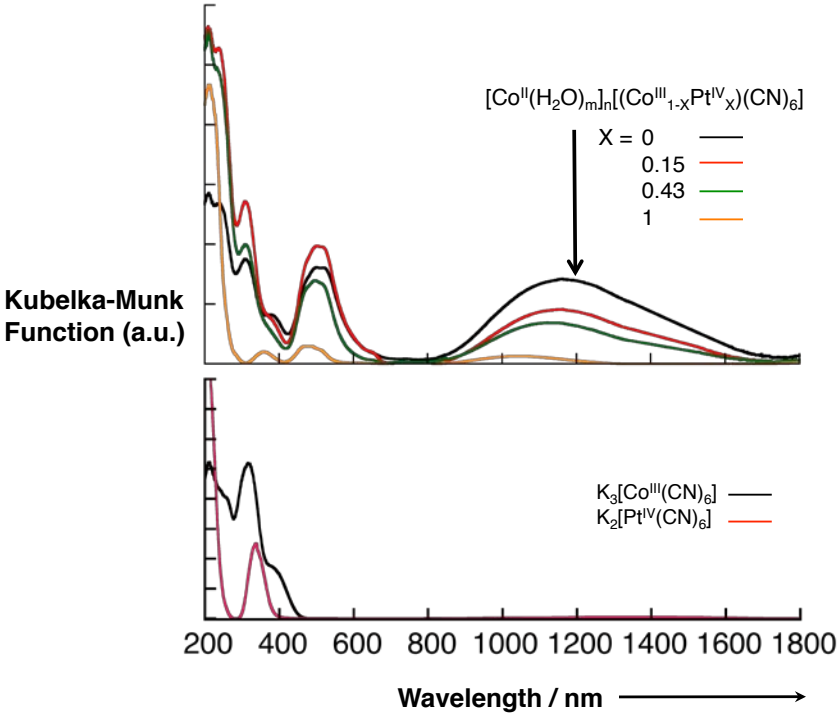

Figure S3. Diffused reflectance UV-vis spectra of top) a series of hetero-polynuclear cyanide complexes, $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$. x = 0 (black); 0.15 (red); 0.43 (green) and 1 (orange) and bottom) $K_3[Co^{III}(CN)_6]$ (black) and $K_2[Pt^{IV}(CN)_6]$ (red).

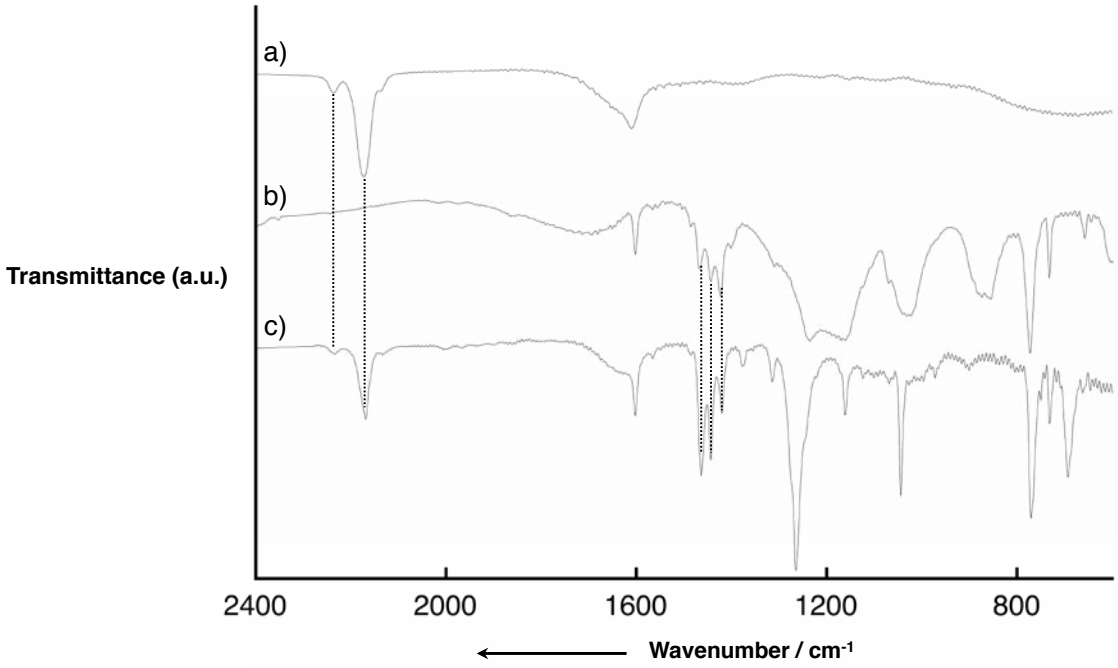

Figure S4. IR spectra of $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}_{0.85}Pt^{IV}_{0.15})(CN)_6]$ a) before and c) after the photocatalytic O_2 evolution and b) $[Ru^{II}(bpy)_3](SO_4)$.

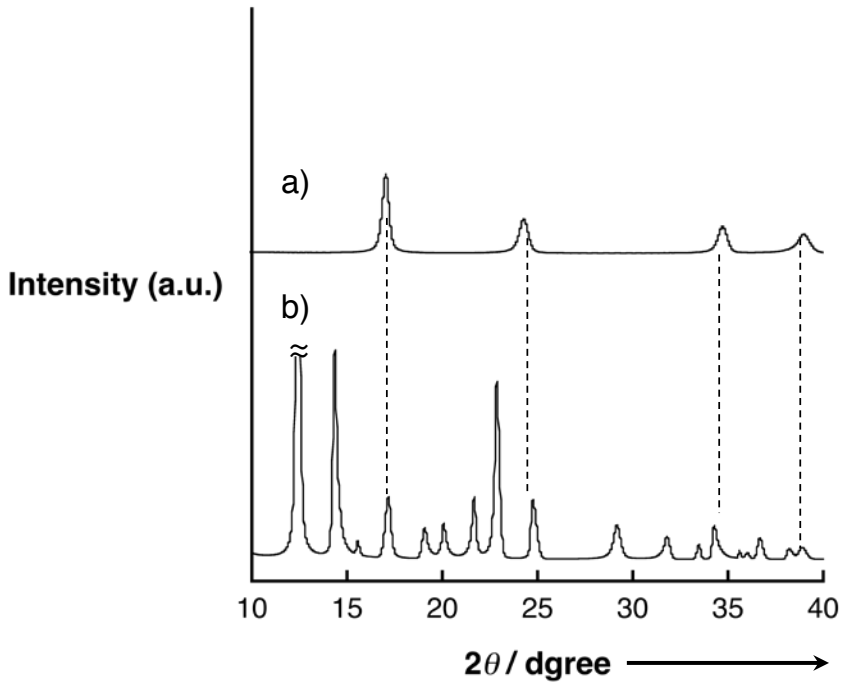

Figure S5. Powder X-ray diffraction patterns of $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}_{0.85}Pt^{IV}_{0.15})(CN)_6]$ before and after the photocatalytic O_2 evolution.

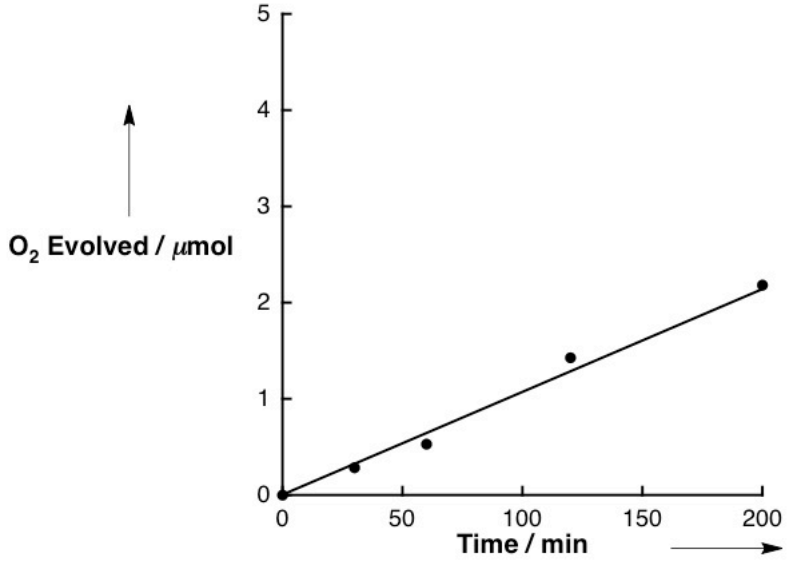

Figure S6. Time course of O_2 evolution by photoirradiation (λ = 450 nm) of a phthalate buffer (2.0 mL) containing $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$ (80 μg), $[Ru(bpy)_3]^{2+}$ (1.0 mM, 1.55 mg), $Na_2S_2O_8$ (5.0 mM, 2.38 mg) in a quartz cuvette (light path length: 1.0 cm).

An apparent quantum yield (Φ) was determined by the following equation [Eq. (1)]:

$\Phi = 2 \times \{\text{mole of } O_2 \text{ evolved}\}/\{\text{photon flux}\}$ (1)

Photon flux was determined using a chemical actinometer as 7.40×10^{-10} einstein s^{-1}.

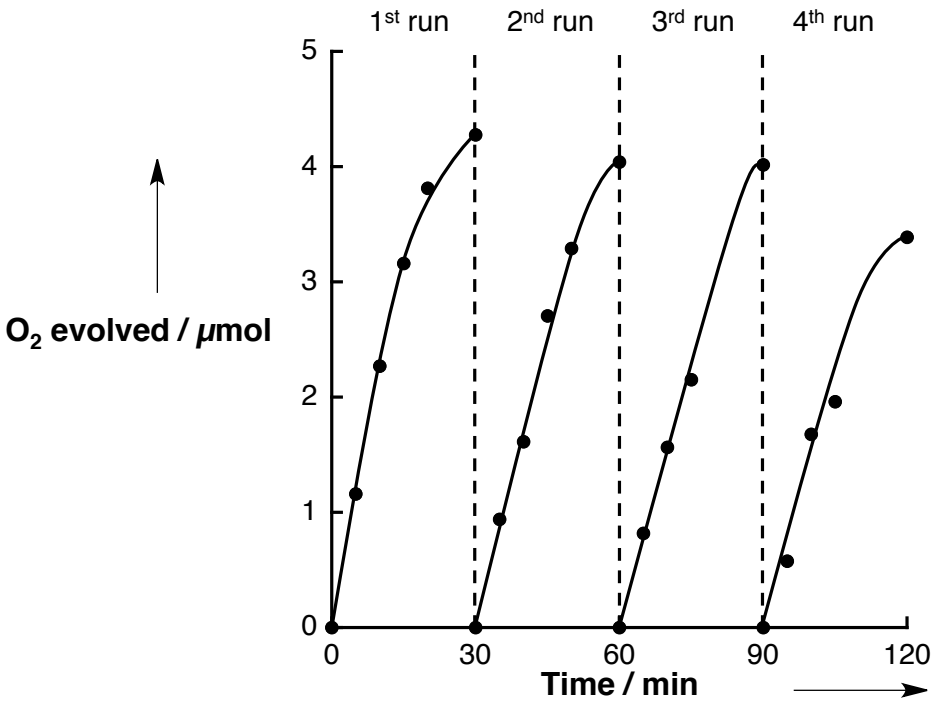

Figure S7. Time courses of O_2 evolution by visible-light irradiation ($\lambda > 420$ nm) of a phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) and a heteropolynuclear cyanide complex, $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$, (800 μg) in the repetitive experiments.

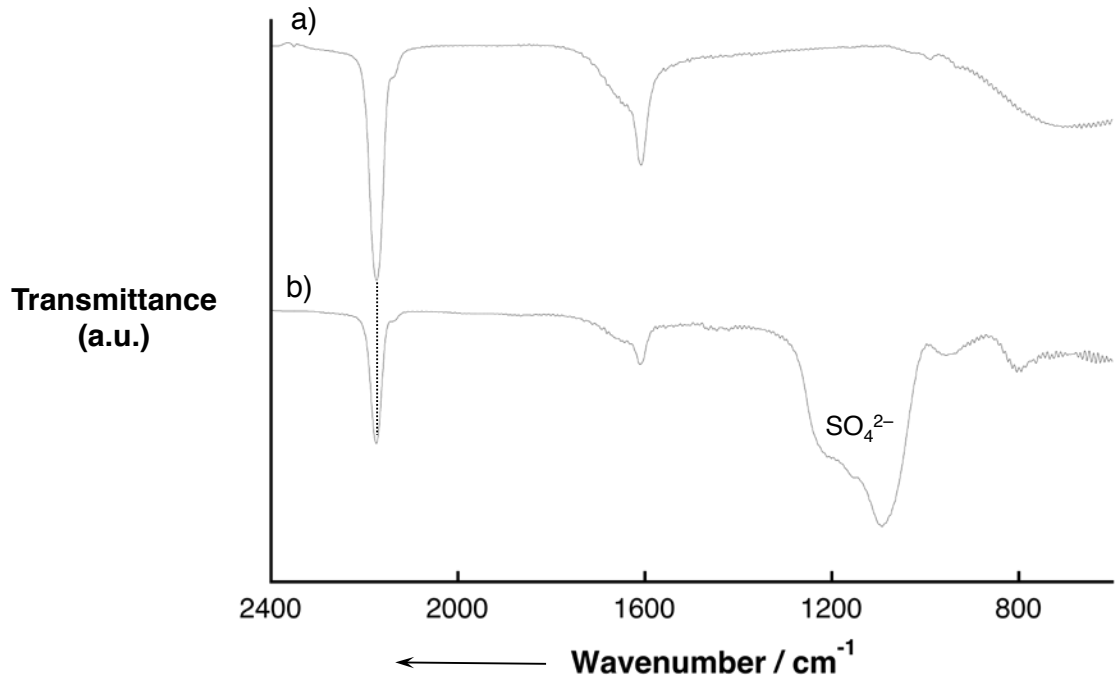

Figure S8. IR spectra of $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$ a) before and b) after the photocatalytic O_2 evolution.

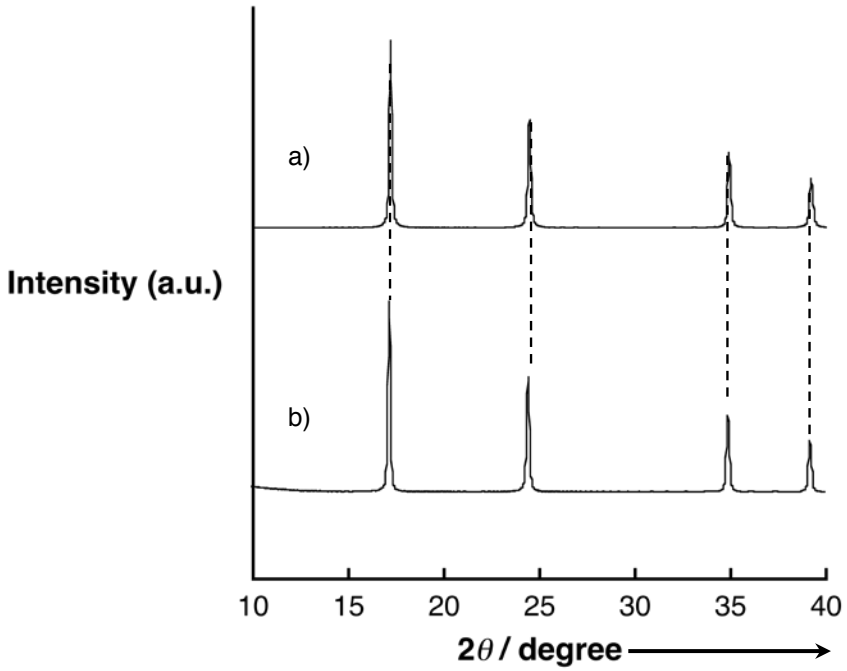

Figure S9. XRD patterns of $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$ a) before and b) after the photocatalytic O_2 evolution.